

# SPECIFICATION

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## METHOD OF DEPOSITION A COMPOSITIONALLY-GRADED COATING SYSTEM

### Federal Research Statement

[Federal Research Statement Paragraph] This invention was made with Government support under Agreement No. F33615-98-C-2893 awarded by the U.S. Department of the Air Force. The Government has certain rights in the invention.

### Background of Invention

#### Field of the Invention

[0001] The present invention generally relates to coating systems suitable for protecting components exposed to high-temperature environments, such as the hostile thermal environment of a gas turbine engine. More particularly, this invention is directed to a process of depositing a graded thermal/environmental barrier coating system on a composite substrate material.

### Description of the Related Art

[0002] Higher operating temperatures for gas turbine engines are continuously sought in order to increase their efficiency. However, as operating temperatures increase, the high temperature durability of the components of the engine must correspondingly increase. Significant advances in high temperature capabilities have been achieved through formulation of iron, nickel and cobalt-base superalloys. While superalloys have found wide use for components throughout gas turbine engines, alternative materials have been proposed. For example, composite materials, particularly silicon-based composites with silicon carbide (SiC) as a matrix and/or as a reinforcing material, are currently being considered for high temperature applications, such as

combustor liners, airfoils, nozzles and other hot section components of gas turbine engines.

[0003] In many high temperature applications, a protective coating is beneficial or required for a Si-containing material. For example, protection with a suitable thermal-insulating layer reduces the operating temperature and thermal gradient through the material. Additionally, such coatings should provide environmental protection by inhibiting the major mechanism for degradation of Si-containing materials in a corrosive water-containing environment, namely, the formation of volatile silicon monoxide ( $\text{SiO}$ ) and silicon hydroxide ( $\text{Si}(\text{OH})_4$ ) products. Consequently, besides low thermal conductivity, a critical requirement of a thermal barrier coating system for a Si-containing material is stability in high temperature environments containing water vapors. Other important properties for the coating material include a coefficient of thermal expansion (CTE) compatible with the SiC-containing material, low permeability for oxidants, and chemical compatibility with the Si-containing material and silica scale formed from oxidation. As a result, suitable protective coatings for turbine engine components formed of Si-containing materials essentially have a dual function, serving as a thermal barrier and simultaneously providing environmental protection. A coating system having this dual function may be termed a thermal/environmental barrier coating (T/EBC) system.

[0004] Various single-layer and multilayer T/EBC systems have been investigated for use on Si-containing substrates. Coatings of zirconia partially or fully stabilized with yttria (YSZ) as a thermal barrier layer exhibit excellent environmental resistance. However, YSZ does not adhere well to Si-containing materials (SiC or silicon) because of a CTE mismatch (about 10 ppm/°C for YSZ as compared to about 4.9 ppm/°C for SiC/SiC composites). Mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) has been proposed as a bond coat for YSZ on Si-containing substrate materials to compensate for this difference in CTE (mullite having a CTE of about 5.5 ppm/°C), though mullite exhibits significant silica activity and volatilization at high-temperatures if water (water vapor) is present. Barium-strontium-aluminosilicate (BSAS) coatings have also been proposed as a protective coating for Si-containing materials in view of its excellent environmental protection properties and low thermal conductivity. In addition, BSAS has been proposed as a bond coat for YSZ in U.S. Patent No. 5,985,970 to Spitsberg et al., assigned to the

assignee of the present invention.

[0005] As application temperatures increase further beyond the thermal capability of a Si-containing material (limited by a melting temperature of about 2560 ° F (about 1404 ° C) for silicon), relatively thick coatings capable of withstanding higher thermal gradients are required. However, as coating thicknesses increase, strain energy due to the CTE mismatch between individual coating layers and the substrate increases as well, which can cause debonding and spallation of the coating system. As a solution, U.S. Patent No. 09/543,956 to Wang et al. discloses a compositionally-graded T/EBC system that exhibits improved mechanical integrity for high application temperatures. The T/EBC system includes an intermediate layer containing YSZ and mullite, alumina and/or an alkaline-earth metal aluminosilicate (preferably BSAS). The intermediate layer is used in combination with a mullite-containing layer that overlies the surface of a Si-containing substrate, a layer of an alkaline-earth metal aluminosilicate (again, preferably BSAS) between the mullite-containing layer and the intermediate layer, and a thermal-insulating topcoat of YSZ overlying the intermediate layer. An optional silicon bond layer may be deposited on the substrate prior to depositing the mullite-containing layer. The mullite-containing layer has a CTE above that of a Si-containing substrate but less than that of the YSZ topcoat, and therefore compensates for the difference in CTE between the Si-containing substrate and the other coating layers. In addition, the mullite-containing layer serves as a chemical barrier between BSAS layer and the Si-containing substrate to prevent interaction of BSAS with the silicon oxidation product ( $\text{SiO}_2$ ) at high temperatures. The BSAS layer provides environmental protection to the silicon-containing substrate, while the YSZ topcoat offers thermal protection to the Si-containing substrate and the other underlying layers of the coating system. Finally, the intermediate layer serves as a thermal barrier layer that also provides a CTE transition between the BSAS layer and the YSZ topcoat as a result of its BSAS, mullite and/or alumina content, each of which has a CTE between that of YSZ and Si-containing materials.

[0006] In view of the above, the compositionally-graded T/EBC disclosed by Wang et al. is able to reliably provide both thermal and environmental protection to a Si-containing substrate at high temperatures. Another desirable feature of the T/EBC of Wang et al. is that each of its ceramic layers can be readily deposited by known deposition

techniques, particularly air plasma spraying. Nonetheless, further improvements are continuously sought. For example, though the coating system taught by Wang et al. makes use of a carefully tailored combination of coating materials, horizontal cracking and spallation has been observed in the intermediate layer and the YSZ topcoat following thermal cycling at high temperatures. Accordingly, it would be desirable if the microstructure and mechanical integrity of this coating system could be enhanced.

## Summary of Invention

[0007] The present invention generally provides a process for depositing a ceramic coating system for Si-containing materials, particularly those for articles exposed to high temperatures, including the hostile thermal environment of a gas turbine engine. Examples of such materials include those with a dispersion of silicon carbide, silicon carbide and/or silicon reinforcement material in a metallic or nonmetallic matrix, as well as those having a silicon carbide, silicon nitride and/or silicon-containing matrix, and particularly composite materials that employ silicon carbide, silicon nitride and/or silicon as both the reinforcement and matrix materials (e.g., SiC/SiC ceramic matrix composites (CMC)).

[0008] The invention is particularly applicable, though not limited, to depositing the compositionally-graded T/EBC system disclosed by Wang et al., and is tailored to improve the mechanical integrity of this T/EBC system when deposited on silicon-containing substrates used in high temperature combustion environments. As such, coatings deposited with this invention comprise multiple ceramic layers with differing compositions, and particularly a dense, strain-tolerant, vertically-cracked YSZ-containing ceramic layer that is deposited on a second ceramic layer having a composition different than the YSZ-containing ceramic layer. Particularly suitable compositions for the second ceramic layer include the intermediate layer disclosed by Wang et al., namely, a layer containing YSZ and mullite, alumina and/or an alkaline-earth metal aluminosilicate (preferably BSAS), and especially a mixture consisting essentially of YSZ and either mullite or BSAS. The method entails depositing the YSZ-containing ceramic layer using a plasma spraying technique while maintaining the silicon-containing substrate at a temperature of not greater than about 600 ° C, and more preferably not higher than about 450 ° C to about 550 ° C, depending on the

composition of the second ceramic layer on which the YSZ-containing ceramic layer is deposited.

[0009] According to this invention, a compositionally-graded T/EBC deposited on a silicon-containing substrate and comprising a dense, strain-tolerant, vertically-cracked YSZ-containing layer deposited on a second ceramic layer containing a mixture of YSZ and BSAS or mullite has been shown to exhibit improved mechanical integrity and thermal cycle fatigue life if the deposition process for the YSZ-containing layer is carefully controlled so that the temperature of the silicon-containing substrate does not exceed about 600 ° C. A particularly suitable temperature for the substrate is about 450 ° C if the second ceramic layer (on which the YSZ-containing layer is deposited) contains YSZ and BSAS, and a particularly suitable temperature for the substrate is about 550 ° C if the second ceramic layer contains YSZ and mullite. Limiting the deposition temperature in this manner has been associated with the avoidance of fine horizontal cracks, which are believed to promote wrinkling and eventually spallation of the T/EBC, while maintaining the desired dense vertically-cracked structure of the YSZ-containing ceramic layer for strain tolerance. Therefore, by limiting the deposition temperature, the microstructure and mechanical integrity of the coating system can be enhanced, leading to a longer component life.

[0010] Other objects and advantages of this invention will be better appreciated from the following detailed description.

### Brief Description of Drawings

[0011] Figure 1 is a cross-sectional representation of a thermal/environmental barrier coating system of the present invention.

[0012] Figure 2 is a scanned image of a cross-sectional view of an as-deposited thermal/environmental barrier coating system containing horizontal cracks.

[0013] Figure 3 is a scanned image of a cross-sectional view of a coating system essentially identical to Figure 1 and following thermal cycling.

[0014] Figure 4 is a scanned image of a cross-sectional view of a thermal/environmental barrier coating system as deposited in accordance with this invention.

[0015] Figure 5 is a scanned image of a cross-sectional view of a thermal/environmental barrier coating system deposited in accordance with this invention and following thermal cycling.

## Detailed Description

[0016] The present invention is generally applicable to components that operate within environments characterized by relatively high temperatures, and are therefore subjected to severe thermal cycling and stresses, oxidation, and corrosion. Notable examples of such components include combustor components, high pressure turbine vanes, and other hot section components of gas turbine engines, though the invention has application to other components.

[0017] Figure 2 is a scanned image of a cross-section of a substrate 10 on which a multilayer T/EBC system 12 has been deposited. The substrate 10 is formed of a SiC/SiC CMC, though the invention is generally applicable to other materials containing silicon in any form. The coating system 12 is representative of the coating system disclosed in U.S. Patent Application Serial No. 09/543,956 to Wang et al., and as such includes a thermal-insulating topcoat 22 that provides environmental protection to the underlying substrate 10 as well as reduces the surface temperature of the substrate 10 and interior layers 14, 16, 18 and 20 of the coating system 12. The preferred material for the topcoat 22 is YSZ, preferably containing about 7 to about 10 weight percent yttria, though it is foreseeable that other ceramic materials could be used. A suitable thickness range for the YSZ topcoat 22 is about 12.5 to about 1250 micrometers (about 0.0005 to about 0.050 inch), with a preferred range of about 125 to about 750 micrometers (about 0.005 to about 0.030 inch), depending on the particular application.

[0018] The major mechanism for degradation of silicon carbide (as well as silicon and other silicon compounds) in a corrosive environment is the formation of volatile silicon monoxide ( $\text{SiO}$ ) and silicon hydroxide ( $\text{Si(OH)}_4$ ) products. The diffusivity of oxidants in the YSZ topcoat 22 is generally very high. Therefore, in order to protect the Si-containing substrate 10, the coating system 12 must include additional layers beneath the topcoat 22 that, individually or in combination, exhibit low diffusivity to oxidants, e.g., oxygen and water vapor, to inhibit oxidation of the silicon carbide

within the substrate 10, while also being sufficiently chemically and physically compatible with the substrate 10 to remain adherent under severe thermal conditions. In Figure 2, these additional layers of the coating system 12 include a layer 16 containing a mixture of mullite and an alkaline-earth metal aluminosilicate, preferably BSAS (hereinafter, mullite/BSAS layer 16), and a layer 18 of an alkaline-earth metal aluminosilicate, again preferably BSAS (hereinafter, BSAS layer 18). Finally, separating the BSAS layer 18 and the topcoat 22 is a YSZ-containing fourth layer 20 that also contains mullite or an alkaline-earth metal aluminosilicate, again preferably BSAS. This fourth layer 20 will be referred to as the transition layer 20 below. In accordance with the teachings of Wang et al., the above combination of interior layers 16, 18 and 20 provides a graded composition that fulfills the requirements noted above.

[0019] The innermost layer seen directly on the substrate 10 in Figure 2 is an optional silicon layer 14. In accordance with U.S. Patent Application Serial No. 09/299,418, the inclusion of the silicon layer 14 is useful to improve oxidation resistance of the substrate 10, and enhances bonding of the mullite/BSAS layer 16 to the substrate 10 if the substrate 10 contains SiC or silicon nitride ( $\text{Si}_3\text{N}_4$ ). A suitable thickness for the silicon layer 14 is about 25 to about 250 micrometers (about 0.001 to about 0.010 inch).

[0020] The mullite/BSAS layer 16 serves to adhere the BSAS and YSZ-containing layers 18 and 20 to the Si-containing substrate 10, while also preventing interactions between the BSAS layer 18 and the Si-containing substrate 10 at high temperatures. Mullite is a desirable constituent of this layer 16 because of its chemical stability with Si-containing materials at high temperatures. The layer 16 preferably contains BSAS (and may even be entirely BSAS) for applications with temperatures below about 1300 °C. The addition of BSAS to the layer 16 is also relatively compatible with the Si-containing substrate 10 in terms of having a CTE of about 5.27 ppm/ °C, as compared to a CTE of about 4.9 ppm/ °C for SiC/SiC CMC. A suitable thickness range for the mullite/BSAS layer 16 is about 25 to about 250 micrometers (about 0.001 to about 0.010 inch), depending on the particular application.

[0021] The BSAS layer 18 overlying the mullite/BSAS layer 16 provides excellent environmental protection and exhibits good thermal barrier properties due to its low

thermal conductivity. Particularly, BSAS is able to serve as an environmental barrier to the underlying mullite/BSAS layer 16, which as a result of its mullite content would exhibit significant silica activity and volatilization if exposed to water vapor at high temperatures. As a result, the BSAS layer 18 is able to inhibit the growth of an interfacial silica layer at the substrate 10 when the component 10 is exposed to the oxidizing environment of a gas turbine engine. In addition, BSAS is physically compliant with a SiC-containing substrate, such as the substrate 10, and is relatively compatible with the mullite/BSAS layer 16 and the Si-containing substrate 10 in terms of CTE. A suitable thickness range for the BSAS layer 18 is about 125 to about 1000 micrometers (about 0.005 to about 0.040 inch), depending on the particular application.

[0022] Finally, according to Wang et al. the transition layer 20 is desirable to promote the ability of the coating system 12 to thermally and environmentally protect the Si-containing substrate 10 over numerous thermal cycles and at elevated temperatures. In a preferred embodiment, the transition layer 20 is a substantially homogeneous mixture of about 50 volume percent YSZ and 50 volume percent of either BSAS or mullite, though other proportions are foreseeable. Alternatively, the transition layer could be made up of discrete sublayers, each with a different composition, or be a continuously changing composition from essentially all YSZ adjacent the YSZ topcoat 22 to essentially all BSAS or mullite adjacent the BSAS layer 18.

[0023] The YSZ constituent of the transition layer 20 serves to increase its overall CTE to something closer to the YSZ topcoat 22. An advantage of using mullite with YSZ in the transition layer 20 includes the high temperature capability of mullite as compared to BSAS. On the other hand, because BSAS exhibits low silica activity and low diffusivity to oxidants, a transition layer 20 that contains BSAS is able to serve as an environmental barrier to the underlying substrate 10. Simultaneously, additions of BSAS to the layer 20 render this layer 20 more compatible with the underlying BSAS layer 18 in terms of CTE. Advantageously, BSAS exhibits sufficient environmental resistance such that, if the YSZ topcoat 22 were to spall, an underlying transition layer 20 containing BSAS could continue to provide a level of environmental protection to the mullite/BSAS layer 16 and Si-containing substrate 10. A suitable thickness for the transition layer 20 is up to about 500 micrometers (up to about 0.020 inch),



depending on its composition, the particular application, and the thickness of the other layers 16, 18 and 22. High application temperatures, e.g., up to 2000 ° C, necessitate thick protective coating systems, generally on the order of 250 micrometers or more. It is with such coating systems that the benefits of the transition layer 20 become particularly important to the mechanical integrity of the coating system 12.

[0024] As with prior art thermal barrier and environmental coatings, the layers 16, 18, 20 and 22 can be individually deposited by air and vacuum plasma spraying (APS and VPS, respectively), though it is foreseeable that deposition could be performed by other known techniques, such as high velocity oxy-fuel (HVOF). Thereafter, a heat treatment may be performed after deposition of the individual layers 16, 18, 20 and 22 to relieve residual stresses created during cooling from elevated deposition temperatures. The coating system 12 shown in Figure 2 was deposited by air plasma spraying.

[0025] In an investigation leading up to the present invention, the microstructure and mechanical integrity of coating systems of the type described above were found to vary considerably. According to the present invention, this variation in microstructure and mechanical integrity was determined to be dependent at least in part on the temperature of the substrate 10, hereinafter the deposition temperature, during the application of the YSZ topcoat 22. For the specimen shown in Figure 2, the YSZ topcoat 22 was deposited at a deposition temperature of about 550 ° C on a 50/50 vol.% YSZ/BSAS transition layer 20. The YSZ topcoat 22 is seen to be dense with vertical cracks that are desirable for improved strain tolerance. However, horizontal cracks 24 (cracks parallel to the surface of the substrate 10) can also be seen within the BSAS layer 18, the transition layer 20 and the YSZ topcoat 22 in the as-deposited condition. Also apparent in Figure 2, the microstructure of the coating system 12 can be seen to have a wrinkled appearance.

[0026] Figure 3 represents an identical coating system after undergoing a high steam cycle furnace (HSCF) test to assess the durability and protective capability of the coating system. During the HSCF test, the specimen was exposed to 250 thermal cycles between room temperature and about 2400 ° F (about 1315 ° C) over a period

of 500 hours in a flowing atmosphere of about 90% H<sub>2</sub>O and about 10% O<sub>2</sub>. In Figure 3, the damage to the microstructure of the coating system is apparent when compared with the microstructure shown in Figure 2. While not wishing to be held to any particular theory, the cracks 24 and wrinkled appearance seen in Figure 2 were believed to be the result of stresses due to thermal expansion mismatch between the layers 16, 18, 20 and 22 during deposition, and that the cracks 24 propagated during thermal cycling, causing the enlarged cracks and spallation seen in Figure 3. As such, the presence of the horizontal cracks 24 was concluded to be detrimental to the mechanical integrity of the coating system, and therefore the protection provided by the coating system.

[0027] In contrast to Figure 2, Figure 4 shows the microstructure of a second coating system 112 on a substrate 110 essentially identical to the substrate 10 of Figures 2 and 3. Also similar to the coating system 12 of Figures 2 and 3, the coating system 112 of Figure 4 includes a silicon layer 114, a mullite/BSAS layer 116, a BSAS layer 118, a 50/50 vol.% YSZ/BSAS transition layer 120, and a dense, strain-tolerant, vertically-cracked YSZ topcoat 122. The coating system 112 of Figure 4 is schematically represented in Figure 1. The specimen shown in Figure 4 was essentially identical to that of Figure 2, except that the YSZ topcoat 122 was deposited on the YSZ/BSAS transition layer 120 at a deposition temperature of about 450 ° C, instead of 550 ° C. From Figure 4, it is apparent that horizontal cracks of any significant size are absent from the BSAS layer 118, the transition layer 120 and the YSZ topcoat 122 in the as-deposited condition, though the desirable vertical cracks are present. Also apparent in Figure 4, the surface of the coating system 112 is smoother than the coating system 12 of Figure 2, corresponding to a smoother surface appearance in contrast to the wrinkled appearance of Figure 2.

[0028] From the above, it was concluded that reducing the deposition temperature to something below about 550 ° C when depositing a YSZ topcoat 122 on a YSZ/BSAS transition layer 120 was necessary to produce a coating system 112 with a strain-tolerant microstructure and enhanced mechanical integrity. While a suitable temperature is about 450 ° C based on this investigation, it was concluded that deposition temperatures of up to about 500 ° C are acceptable when depositing YSZ on a transition layer containing a mixture of YSZ and BSAS or another alkaline-earth

metal aluminosilicate. A minimum deposition temperature of about 300 ° C is believed to be necessary for there to occur localized remelting and formation of a coherent columnar structure within the YSZ topcoat 122, in accordance with the teachings of commonly-assigned U.S. Patent Nos. 5,830,586 and 6,180,184 to Gray et al.

[0029] Figure 5 shows the microstructure of a T/EBC system after HSCF testing under the same conditions as those experienced by the specimen shown in Figure 3. For this specimen, a dense, strain-tolerant, vertically-cracked YSZ topcoat was deposited at a deposition temperature of about 550 ° C on a 50/50 vol.% YSZ/mullite transition while the remaining layers are essentially identical to the specimens of Figures 2 through 4. Similar to the specimen of Figure 4, in the as-coated condition the BSAS layer, the transition layer and the YSZ topcoat were free of horizontal cracks of any significant size, though the desirable vertical cracks are present. The coating system also did not have a wrinkled appearance prior to testing. Finally, Figure 5 evidences that the deposition process by which the coating system was formed did not result in the development of large horizontal cracks or spallation during thermal cycling. Accordingly, it was concluded that, though unacceptable when depositing a YSZ topcoat on a YSZ/BSAS transition layer (as done in Figure 4), a deposition temperature of about 550 ° C was acceptable for a coating system having a transition layer containing YSZ and mullite. It was subsequently concluded that deposition temperatures of less than 600 ° C would be acceptable when depositing YSZ on a YSZ/mullite transition layer, in terms of producing a strain-tolerant microstructure with enhanced mechanical integrity. As with coating systems utilizing a YSZ/BSAS transition layer, a minimum deposition temperature of 300 ° C is believed to be a required when depositing YSZ on a YSZ/mullite transition layer.

[0030] At this point, it should be noted that commonly-assigned U.S. Patent Nos. 5,830,586 and 6,180,184 to Gray et al. disclose a thermal barrier coating (TBC) with a coherent, columnar microstructure comprising multiple layers of YSZ deposited by plasma spraying while maintaining a deposition temperature in the range of about  $0.2T_m$  (about 300 ° C for YSZ) to about  $0.5T_m$  (about 1200 ° C for YSZ), where  $T_m$  is the absolute melting temperature of the material (e.g., YSZ) being deposited. The YSZ TBC is deposited on a metallic bond coat, and each YSZ layer is said to cause localized remelting of the underlying deposition (YSZ) surface, resulting in the entire TBC

having a coherent columnar structure if the deposition temperature is in the range of about  $0.2T_m$  to  $0.5T_m$ . The degree of columnarity is expected to increase with increasing deposition surface temperature with an onset temperature of about  $0.2T_m$  (about  $300^\circ\text{C}$  for YSZ). This coherent columnar structure is critical to the strain tolerant capability of the TBC. In any event, Gray et al. advocate higher deposition temperatures, preferably  $600^\circ\text{C}$  or higher (about  $0.29T_m$  for YSZ). In the present invention, a high deposition temperature, e.g., above  $450^\circ\text{C}$  for deposition of a YSZ topcoat 22 on a YSZ/BSAS transition layer 20, was determined to cause undesirable horizontal cracks in the underlying coating layers 16, 18 and 20, which was attributed to the CTE mismatch of the YSZ topcoat 22 with the underlying coating layers 16, 18 and 20. According to the present invention, to deposit a strain-tolerant YSZ top coat 122 with a coherent columnar structure and without undesirable horizontal cracks, the deposition temperature must be at least  $300^\circ\text{C}$  and not significantly higher than about  $450^\circ\text{C}$  or about  $550^\circ\text{C}$ , depending on the composition of the transition layer 120. Such limitations are contrary to the teachings of Gray et al., who teach that deposition temperatures of  $600^\circ\text{C}$  and higher are beneficial for the coating system taught by Gray et al.

[0031] While the invention has been described in terms of a preferred embodiment, it is apparent that other forms could be adopted by one skilled in the art. Accordingly, the scope of the invention is to be limited only by the following claims.